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**Japanese Patent Application JP 2000 - 136294 A**

**Amorphous Polyethylene Terephthalate Resin Composition  
and Calendering Method Thereof**

**Your Ref: 103003 - 13**

**For: Eastman Chemical Company**

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**(54) [Title of the Invention]**

**Amorphous Polyethylene Terephthalate Resin  
Composition and Calendering Method Thereof**

**(57) [Summary]**

**[Object]** To provide an amorphous polyethylene terephthalate sheet resin composition and a processing method thereof whereby a sheet material that has excellent surface smoothness and can be easily released from metal rolls can be obtained by means of calendering.

**[Means of Achievement]** The aforementioned resin composition is a substance in which one or both of 0.1 to 15 parts by weight of acrylic acid resin with a weight-average molecular weight of 50,000 to 6,000,000 and 0.05 to 2 parts by weight of tetrafluoroethylene-modified acrylic acid resin are compounded per 100 parts by weight of amorphous polyethylene terephthalate resin.

**[Claims]**

**[Claim 1]** An amorphous polyethylene terephthalate resin composition characterized in that one or both of 0.1 to 15 parts by weight of acrylic acid resin with a weight-average molecular weight of 50,000 to 6,000,000 and 0.05 to 2 parts by weight of tetrafluoroethylene-modified acrylic acid resin are compounded per 100 parts by weight of amorphous polyethylene terephthalate resin.

**[Claim 2]** An amorphous polyethylene terephthalate resin composition as described in Claim 1, wherein at least one of titanium oxide, talc, and calcium carbonate is compounded in an amount of 1 to 20 parts by weight.

**[Claim 3]** An amorphous polyethylene terephthalate resin composition as described in Claim 1, wherein the acrylic acid resin with a weight-average molecular weight of 50,000 to 6,000,000 is composed of a combination of two types, that is, 0.2 to 10 parts by weight of acrylic acid resin with a weight-average molecular weight of 50,000 to 700,000 and 0.1 to 5 parts by weight of acrylic acid resin with a weight-average molecular weight of 700,000 to 6,000,000.

**[Claim 4]** A method of calendering an amorphous polyethylene terephthalate resin composition, characterized in that the composition is processed using a calendering device equipped with four or more metal rolls, and the surface temperature of the final roll is 80 to 160°C higher than the glass transition temperature of the amorphous polyethylene terephthalate resin composition.

**[Detailed Description of the Invention]**

**[0001]**

**[Technological Field of the Invention]** The present invention relates to an amorphous polyethylene terephthalate resin composition of superior calendering properties and to a processing method thereof.

**[0002]**

**[Prior Art]** Polyethylene terephthalate is commonly used as a packaging material for food products and industrial materials, and as lamination sheets for buildings, household electrical

products, and automobiles. The polyethylene terephthalate used in these applications is conventionally manufactured by means of extrusion molding and injection molding. Extrusion molding and injection molding are processing methods in which a die is adjusted to a specified height, molten resin is discharged, and the material is taken off while rapidly cooled from the softening temperature of the resin. While the sheet can be easily released from the takeoff rolls and the mold, uniform discharge of the molten resin may still be impaired by a poor adjustment in the die and the effects of the resin and additives deposited on the die, often resulting in the formation of regions with marked by local thickness variations in the transverse direction of the die. Sheets in which there are regions with local thickness variations are not suited for printing, lamination, coating, or other types of processing. In addition, such variations cause holes to develop in the sheets when they are subsequently molded into blister packs, trays, and carrier tapes.

[0003] In contrast to these methods, calendering is a process in which molten resin is calendered by means of heated metal rolls to make a sheet of a specified thickness. This method provides superior sheet productivity, and because the material is calendered with rolls, the method is also advantageous in that no difficulties are encountered due to the die or the like, and that there are only a few localized thickness irregularities. However, when amorphous polyethylene terephthalate resin is used as the calendered material, the sheet cannot be easily released from the metal rolls, and actual implementation is difficult.

[0004]

**[Problems to Be Solved by the Invention]** Consequently, the objective of this invention is to provide an amorphous polyethylene terephthalate sheet resin composition and a processing method thereof whereby a sheet material that has excellent surface smoothness and can be easily released from metal rolls can be obtained by means of calendering.

[0005]

**[Means Used to Solve the Above-Mentioned Problems]** The amorphous polyethylene terephthalate resin composition of this invention is a substance in which one or both of 0.1 to 15 parts by weight of acrylic acid resin with a weight-average molecular weight of 50,000 to 6,000,000 and 0.05 to 2 parts by weight of tetrafluoroethylene-modified acrylic acid resin are

compounded per 100 parts by weight of amorphous polyethylene terephthalate resin. Therefore, sheets can be easily processed by means of calendering, and the stated object can be attained.

[0006] Further, calenderability and surface smoothness can be improved by means of compounding 1 to 20 parts by weight of at least one of titanium oxide, talc, and calcium carbonate with the amorphous polyethylene terephthalate resin composition. It is further desirable that the acrylic acid resin be a combination of 0.2 to 10 parts by weight of acrylic acid resin with a weight-average molecular weight of 50,000 to 700,000 and of 0.1 to 5 parts by weight of acrylic acid resin with a weight-average molecular weight of 700,000 to 6,000,000. By this means, sheets can be released with greater ease from the metal rolls of the calender, and surface smoothness can be improved.

[0007] The amorphous polyethylene terephthalate resin composition can be calendered using a calendering device equipped with four or more metal rolls and by means of setting the surface temperature of the final metal rolls within a temperature range 80 to 160°C higher than the glass transition temperature of the amorphous polyethylene terephthalate resin composition. By means of this processing method, the aforementioned amorphous polyethylene terephthalate resin composition can be processed to any desired thickness, and sheets of uniform thickness and superior surface smoothness can be produced very economically. The sheets that are obtained can be used without problems for printing, lamination, and coating, and molded products without holes can be obtained by means of secondary molding.

[0008]

**[Embodiment of the Invention]** The amorphous polyethylene terephthalate that is used in the amorphous polyethylene terephthalate resin composition of this invention should be a substance that is composed of 100 mol% of terephthalic acid, 30 to 90 mol% of ethylene glycol, and 10 to 70 mol% of 1,4-cyclohexane dimethanol, and, more preferably, of 100 mol% of terephthalic acid, 65 to 80 mol% of ethylene glycol, and 20 to 35 mol% of 1,4-cyclohexane dimethanol. When the ethylene glycol component is less than 30 mol% or the 1,4-cyclohexane dimethanol component exceeds 90 mol%, recrystallization of the polyethylene terephthalate resin is promoted and calendering cannot be performed. Conversely, when the ethylene glycol component exceeds 90 mol% or the 1,4-cyclohexane dimethanol component is less than 10 mol%, calendering cannot be performed due to recrystallization.

[0009] The acrylic acid resin that is used in the amorphous polyethylene terephthalate resin composition is a polymer of acrylic acid compounds and methacrylic acid compounds as described in "Independent Regulation Standards Relating to Food Product Container Packaging Manufactured of Polyvinyl Chloride." They can include, for example, polyacrylic acid esters, polymethacrylic acid esters, acrylic acid-methacrylic acid copolymers, copolymers of acrylic acid esters and methacrylic acid esters, copolymers of one or both of acrylic acid esters and methacrylic acid esters, and one or more of the monomers listed below. These monomers can include acrylic acid, glycidyl methacrylate, acrylonitrile, vinyl chloride, butadiene, vinyl acetate, vinylidene chloride, itaconic acid, itaconic acid dibutyl ester, styrene, methacrylic acid,  $\alpha$ -methylstyrene, and cyclohexylmaleimide.

[0010] The acrylic acid resins are substances with weight-average molecular weights in the range of 50,000 to 6,000,000, and are compounded in amounts of 0.1 to 15 parts by weight per 100 parts by weight of the amorphous polyethylene terephthalate resin. It is further desirable that these acrylic acid resins be combinations of two types; that is, acrylic acid resins of weight-average molecular weights of 50,000 to 700,000 in amounts of 0.2 to 10 parts by weight, and, preferably, 0.5 to 5 parts by weight, and acrylic acid resins of weight-average molecular weights of 700,000 to 6,000,000 in amounts of 0.1 to 5 parts by weight, and, preferably, 0.2 to 3 parts by weight.

[0011] When the weight-average molecular weight of the acrylic acid resin is less than 50,000, the rubber elasticity of the fused or softened sheet is decreased, and the sheet that has been released from the metal rolls of the calender elongates and is more difficult to take off. When the weight-average molecular weight exceeds 6,000,000, the sheet cannot be released from the metal rolls of the calender. Further, when the quantity added is less than 0.1 parts by weight, there is no effect on the release from the metal rolls of the calender, and calendering is difficult to accomplish. When the quantity exceeds 15 parts by weight, the material cannot be released as easily from the metal rolls, the strike-through of the calendered resin on the metal rolls is impaired, and stable processing becomes difficult to accomplish. In addition, rotation of the fused resin that has been calendered is not uniform and the surface smoothness of the sheet that is obtained is poor.

[0012] On the other hand, the tetrafluoroethylene-modified acrylic acid resin used herein is obtained by means of copolymerizing acrylic acid or methacrylic acid polymers and tetra-

fluoroethylene. The quantity added is 0.05 to 2 parts by weight, and, preferably, 0.3 to 1 part by weight, per 100 parts by weight of amorphous polyethylene terephthalate resin. When the quantity added is less than 0.05 parts by weight, the rubber elasticity of the fused or softened sheet is decreased, and it is difficult to elongate and draw sheets released from the metal rolls of the calender. When the quantity exceeds 2 parts by weight, the rubber elasticity of the sheet is too high, for which reason the surface is rough and does not have adequate smoothness.

[0013] Compounding one or two or more of titanium oxide, talc, and calcium, which are widely used as pigments or fillers, with the aforementioned amorphous polyethylene terephthalate resin compositions in amounts of 1 to 20 parts by weight, and, preferably, 2 to 10 parts by weight, per 100 parts by weight of amorphous polyethylene terephthalate resin, has the effect of improving the bank rotation of the calender and prevents air from penetrating into the resin sheet. This makes it easier to prevent and regulate the penetration of air into sheets, which is ordinarily achieved by means of varying the temperature and speed ratios of the individual rolls of the calender. When the quantity added is less than 1 weight %, there is little effect in preventing penetration of air into the resin sheet. When the quantity exceeds 20 parts by weight, calendering becomes difficult.

[0014] In addition to the materials described above, desired types and quantities of stabilizers, surfactants, antioxidants, antistatic agents, fillers, ultraviolet absorbers, and pigments can be selected and added as needed to the amorphous polyethylene terephthalate resin composition as long as its calenderability is not impaired.

[0015] In the method for calendering the amorphous polyethylene terephthalate resin composition in accordance with this invention, a calendering device equipped with four or more metal rolls is used and processing is performed with the surface temperature of the final metal roll set to 80 to 160°C higher, and, preferably, 100 to 140°C higher, than the glass transition temperature of the amorphous polyethylene terephthalate resin composition, making it possible to obtain amorphous polyethylene terephthalate sheets of superior surface smoothness. When the surface temperature of the final metal roll is less than the glass transition temperature + 80°C of the amorphous polyethylene terephthalate resin composition, the sheet surface is rough and has inadequate smoothness. Conversely, when the temperature is more than 160°C greater than the glass transition temperature of the amorphous polyethylene terephthalate resin composition, the sheet becomes more difficult to release from the metal rolls.



[0016]

[Working Examples] We shall now describe specific embodiments of the invention by presenting working examples and comparative examples.

Working Examples 1 to 8 and Comparative Examples 1 to 12

The materials described below were compounded in the proportions shown in Table 1 and Table 2 with 100 parts by weight of amorphous polyethylene terephthalate resin, and the resulting compound was mixed to a homogeneous state with a Henschel mixer. The compositions that were obtained were processed to sheets of 0.3 mm in thickness and 1000 mm in width using a reverse L-type calendering device with 4 rolls. The surface temperatures of the metal rolls of the calender were varied, with the first roll, starting from the roll for introducing the resin composition in the molten state, being set to 200°C, the second roll to 200°C, the third roll to 195°C, and the final rolls set to 140°C, 190°C, and 250°C. Evaluations were made of metal roll release properties, surface smoothness of the sheets obtained, and the ease with which the sheet could be taken off from the final metal rolls of the calender on the basis of the standards indicated below. The results are shown in Table 1 and Table 2.

[0017] (Materials used)

- Amorphous polyethylene terephthalate resin PETG 6763 (brand name, manufactured by the Eastman Chemical Co.; amorphous polyethylene terephthalate resin composed of 100 mol% of terephthalic acid, 65 to 70 mol% of ethylene glycol, and 30 to 35 mol% of 1,4-cyclohexane dimethanol; glass transition temperature: 80°C)

- Acrylic acid resin L-1000 (brand name, manufactured by the Mitsubishi Rayon Company; weight-average molecular weight: 200,000)

- Acrylic acid resin P-550A (same as above; weight-average molecular weight: 1,000,000)

- Materials polymerized by means of conventionally known methods were used as the acrylic acid resins with weight-average molecular weights of 10,000 and 8,000,000.

- Tetrafluoroethylene-modified acrylic acid resin A-3000 (same as above; indicated in the tables as fluoroethylene-modified acrylic acid resin)

[0018] (Evaluation Methods)

- Ease of release from the metal rolls of the calender (in the table, indicated as metal roll release properties):

Release of molten, softened sheet from the metals rolls was extremely good    ⊙

Release of molten, softened sheet from the metals rolls was good    ○

Release of molten, softened sheet from the metals rolls was poor    ×

[0019] · Surface smoothness of the sheet (indicated in the table as sheet surface smoothness):

Surface of the sheet was extremely smooth    ⊙

Surface of the sheet was smooth    ○

Surface of the sheet was rough and not smooth    ×

[0020] · Sheet takeoff properties (in the table, indicated as sheet takeoff properties):

Sheet released from the final metal rolls of the calender was moderately elongated, and  
takeoff was extremely easy    ⊙

Sheet released from the final metal rolls of the calender was moderately elongated, and  
takeoff was easy    ○

Because the sheet released from the final metal rolls of the calender was extremely  
elongated, and takeoff was difficult    ×

[0021] The weight-average molecular weight was measured at 40°C by means of the GPC method using tetrahydrofuran as the solvent and using a Syodex GPC KF-800P (brand name, manufactured Showa Denko, protected) and Syodex GPC KF-806F (same as above, analysis) with a Shodex GPC System 11 measurement apparatus (same as above) and with standard polystyrene (manufactured by Water Associates Co.) for the calibration curve.

[0022]

Table 1

			Working Examples								
			1	2	3	4	5	6	7	8	9
Materials and compounding	Acrylic acid resin	Weight-average molecular weight	200 th	200 th	—	200 th	200 th	200 th	200 th	200 th	200 th
		Number of parts added (parts by weight)	3	3	0	3	3	3	3	3	5
		Weight-average molecular weight	1 mln	-	-	1 mln	1 mln	1 mln	1 mln	1 mln	-
		Number of parts added (parts by weight)	1	0	0	0.5	1	1	1	1	0
	Fluoroethylene-modified acrylic acid ester ( $\eta$ )		0	0	1	0.5	0	0	0	0	0.5
		(parts by weight)	0	0	0	0	5	0	0	2	0
Surface temperature of final metal roll in calender (°C)	Titanium oxide	(parts by weight)	0	0	0	0	0	5	0	0	0
	Talc	(parts by weight)	0	0	0	0	0	5	0	1	0
	Calcium carbonate	(parts by weight)	0	0	0	0	0	0	5	1	0
			190	190	190	190	190	190	190	190	190
Results of evaluation	Metal roll release properties		⊙	○	○	⊙	⊙	⊙	⊙	⊙	⊙
		Sheet surface smoothness	○	⊙	○	○	⊙	⊙	⊙	⊙	○
		Sheet takeoff properties	⊙	○	○	⊙	⊙	⊙	⊙	⊙	⊙

th = thousand; mln = million

[0023]

[Table 2]

		Comparative Examples										
		1	2	3	4	5	6	7	8	9	11	12
Materials and com-pounding	Weight-average molecular weight	10 th	8 mln	200 th	200 th	-	-	200 th	200 th	200 th	200 th	200 th
	Number of parts added (parts by weight)	1	0.5	0.05	20	0	0	3	3	3	3	3
	Weight-average molecular weight	-	-	-	-	-	-	1 mln	1 mln	1 mln	1 mln	1 mln
	Number of parts added (parts by weight)	0	0	0	0	0	0	1	1	1	1	1
	Fluoroethylene-modified acrylic acid ester ( $\eta$ )	0	0	0	0	0.01	5	0	0	0	0	0
Surface temperature of final metal roll in calender (°C)	Titanium oxide (parts by weight)	0	0	0	0	0	0	0	0	30	0	0
	Talc (parts by weight)	0	0	0	0	0	0	0	0	0	30	0
	Calcium carbonate (parts by weight)	0	0	0	0	0	0	0	0	0	0	30
Surface temperature of final metal roll in calender (°C)		190	190	190	190	190	190	140	250	190	190	190
Results of evaluation	Metal roll release properties	0	x	x	⊙	0	0	0	x	x	x	x
	Sheet surface smoothness	⊙	0	⊙	x	0	x	x	0	0	0	0
	Sheet takeoff properties	x	⊙	0	0	x	⊙	⊙•	x	0	0	0

th = thousand; mln = million

[0024]

[Effect of the Invention] The amorphous polyethylene terephthalate resin composition of this invention, when calendered, exhibits good metal roll release properties, provides the released sheet with reduced elongation, and can be taken off easily from the final metal roll of the calender. Further, the sheet that is obtained is a high quality sheet-shaped material that is of superior surface smoothness and minimal localized thickness variations. There is also superior productivity. Using this sheet-shaped material can prevent holes from being formed in the sheet due to localized variations in thickness during vacuum molding and pressure vacuum molding, and can also prevent wrinkles from being formed during lamination, paint from being shed during coating, and the like.

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